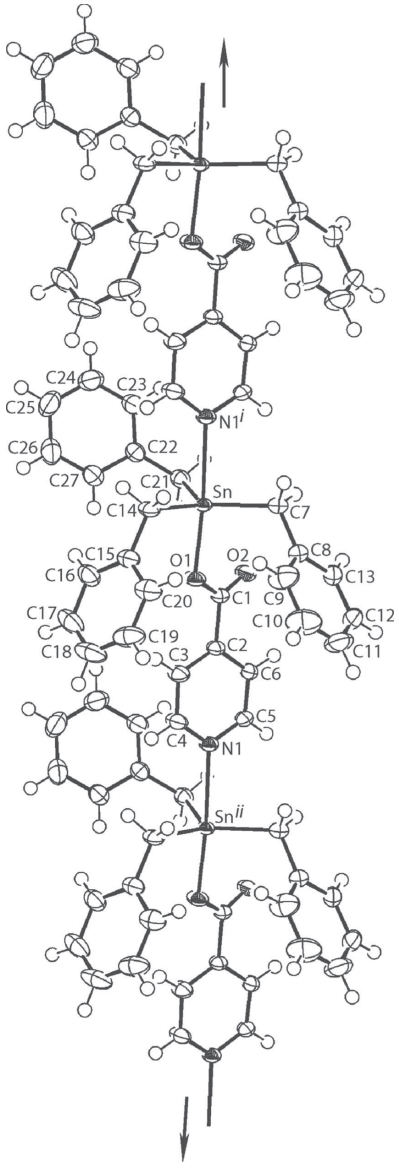
See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Redetermination of the crystal structure of *catena*-poly[[tribenzyltin(IV)]-(μ_2-pyridine-4-carboxylato-κ^2N:O)], $C_{27}H_{25}NO_2Sn$



***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com. https://orcid.org/0000-0003-1401-1520

See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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Abstract

$C_{27}H_{25}NO_2Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 9.61670(10)$ Å, $b = 16.3285(2)$ Å, $c = 14.5921(2)$ Å, $\beta = 97.6430(10)°$, $V = 2270.99(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0221$, $wR_{ref}(F^2) = 0.0566$, $T = 296(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.26 × 0.10 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.15 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
θ_{max}, completeness:	30.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24990, 6662, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6005
$N(param)_{refined}$:	280
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

A part of the title coordination polymer is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

General: The melting point (uncorrected) of the compound was measured on an Electrothermal digital melting point apparatus. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me_4Si.

Synthesis: Tribenzyltin chloride was prepared from the direct synthesis method [6] using tin powder (Sigma-Aldrich) and benzyl chloride (Sigma-Aldrich) in water. Isonicotinic acid (Sigma-Aldrich; 0.12 g, 1.0 mmol) dissolved in ethanol

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.46556(2)	0.34533(2)	0.62306(2)	0.01544(4)
O1	0.68633(11)	0.32862(7)	0.62347(8)	0.0224(2)
O2	0.70526(11)	0.44867(6)	0.55155(8)	0.0228(2)
N1	1.20316(13)	0.35298(7)	0.62174(9)	0.0178(2)
C1	0.75589(14)	0.38702(9)	0.59054(10)	0.0178(3)
C2	0.91246(14)	0.37383(9)	0.60328(10)	0.0167(3)
C3	0.97249(15)	0.29745(10)	0.62331(12)	0.0240(3)
H3	0.916641	0.252145	0.631098	0.029*
C4	1.11679(16)	0.29003(9)	0.63144(12)	0.0246(3)
H4	1.156095	0.238589	0.644336	0.030*
C5	1.14439(15)	0.42656(9)	0.60260(11)	0.0195(3)
H5	1.202582	0.470917	0.595311	0.023*
C6	1.00103(15)	0.43935(9)	0.59323(11)	0.0191(3)
H6	0.964331	0.491407	0.580311	0.023*
C7	0.47402(15)	0.45431(9)	0.70675(12)	0.0234(3)
H7A	0.454171	0.501081	0.666136	0.028*
H7B	0.400020	0.451221	0.745767	0.028*
C8	0.61033(15)	0.46957(9)	0.76731(11)	0.0208(3)
C9	0.6595(2)	0.41639(12)	0.83873(14)	0.0368(4)
H9	0.607963	0.369730	0.848489	0.044*
C10	0.7844(2)	0.43177(15)	0.89583(14)	0.0449(5)
H10	0.816092	0.395351	0.943004	0.054*
C11	0.86127(19)	0.50120(14)	0.88243(14)	0.0389(4)
H11	0.943911	0.512260	0.921221	0.047*
C12	0.81479(18)	0.55385(11)	0.81135(13)	0.0306(4)
H12	0.866984	0.600246	0.801644	0.037*
C13	0.69077(16)	0.53829(9)	0.75407(11)	0.0225(3)
H13	0.660908	0.574306	0.706102	0.027*
C14	0.44879(14)	0.22642(9)	0.68671(11)	0.0199(3)
H14A	0.406328	0.233803	0.742835	0.024*
H14B	0.385521	0.192858	0.645107	0.024*
C15	0.58387(15)	0.18038(9)	0.71066(12)	0.0224(3)
C16	0.63618(18)	0.12925(10)	0.64640(13)	0.0277(3)
H16	0.585333	0.122494	0.588070	0.033*
C17	0.76327(19)	0.08826(10)	0.66839(15)	0.0348(4)
H17	0.797266	0.055258	0.624416	0.042*
C18	0.83880(18)	0.09639(11)	0.75491(15)	0.0368(4)
H18	0.923968	0.069293	0.769294	0.044*
C19	0.78765(19)	0.14476(12)	0.81994(15)	0.0352(4)
H19	0.837323	0.149326	0.878911	0.042*
C20	0.66161(17)	0.18702(11)	0.79786(12)	0.0284(3)
H20	0.628948	0.220215	0.842182	0.034*
C21	0.41066(16)	0.35365(9)	0.47559(11)	0.0201(3)
H21A	0.359488	0.404155	0.460729	0.024*
H21B	0.495840	0.355694	0.446756	0.024*
C22	0.32292(16)	0.28294(9)	0.43653(10)	0.0199(3)
C23	0.18223(17)	0.29149(10)	0.40092(12)	0.0271(3)
H23	0.140865	0.343030	0.399726	0.032*
C24	0.10232(19)	0.22456(12)	0.36709(13)	0.0348(4)
H24	0.008408	0.231665	0.343494	0.042*
C25	0.1618(2)	0.14728(11)	0.36833(14)	0.0360(4)
H25	0.108228	0.102420	0.345834	0.043*
C26	0.3017(2)	0.13742(11)	0.40335(13)	0.0327(4)
H26	0.342489	0.085745	0.404332	0.039*
C27	0.38106(18)	0.20441(10)	0.43696(11)	0.0249(3)
H27	0.474993	0.196993	0.460304	0.030*

(30 mL) and tribenzyltin chloride (0.41 g, 1 mmol) in chloroform (15 mL) were heated for 1 h. After filtration, the filtrate was evaporated slowly to obtain a white crystalline solid. Yield: 0.41 g (80%). M. pt: 433−435 K. Calcd for $C_{27}H_{25}NO_2Sn$: C 63.07; H 4.90; N 2.72%. Found: C 62.91; H 4.85; N 2.71%. IR (cm^{-1}): 452 (*m*) ν(Sn−N), 571 (*m*) ν(Sn−O), 1645 (*s*) ν_{asym}(COO), 1354 (*s*) ν_{sym}(COO), 1559 (*s*) ν(C=N). ^{1}H NMR ($CDCl_3$, p.p.m.): δ 7.48−8.61 (4*H*, pyridine-H), 6.92−7.12 (15*H*, Ph−H), 2.60 (6*H*, Ph−CH_2).

Experimental details

The C-bound H atoms were geometrically placed (C−H = 0.93−0.97 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). Owing to poor agreement, the (2 0 0) and (9 16 2) reflections were omitted from the final cycles of refinement.

Discussion

The structural chemistry of organotin carboxylates is well established to present a fascinating array of structural motifs [7]. Of relevance to the present study, triorganotin carboxylates, $R_3Sn(O_2CR')$ are usually zero-dimensional, whereby the tin atom is distorted tetrahedral within a C_3O donor set, or one-dimensional, owing to the presence of μ_2-bridging carboxylate ligands with the resulting five-coordinate tin atoms having a *trans*-C_3O_2 donor set [7]. The adoption of one motif over the other is often ascribed to steric effects so that polymeric species with tin-bound (bulky) *R* = cyclohexyl are rarely observed for mono-functional carboxylates and, conversely, the overwhelming majority of structures with, *e.g.* (small) *R* = methyl, are polymeric [7]. Variations to the above occur when the *R′* substituent of the carboxylate ligands carry additional groups capable of coordination, *e.g.* a pyridyl-nitrogen atom, as in the title compound. Additional interest in metal complexes of pyridyl-derived carboxylic acids is encouraged by the reports on the potential biological activities of these compounds [8, 9]. Following a recent report on the enhanced anti-cancer potential of tribenzyltin carboxylates [10], the title compound, $[(benzyl)_3Sn(O_2CC_5H_4N\text{-}4)]_n$, was investigated crystallographically.

The polymeric structure of $[(benzyl)_3Sn(O_2CC_5H_4N\text{-}4)]_n$ has been determined previously but the three-dimensional atomic coordinates are not available [11]. The structure is a linear, one-dimensional coordination polymer as illustrated in the figure (70% displacement ellipsoids; symmetry operations i: −1 + *x*, *y*, *z* and ii: 1 + *x*, *y*, *z*). The chain is propagated by translational symmetry along the *a* axis. The tin atom exists within a *trans*-C_3NO donor set defined by the carbon atoms derived from the three benzyl substituents, an oxygen atom from the carboxylate group and a pyridyl-nitrogen atom

from a symmetry-related pyridine-4-carboxylate ligand. The O1—Sn—N1^{i} angle is 175.49(4)°. This, coupled with the C—Sn—C angles lying in the narrow range of 117.58(6)°, for C7—Sn—C21, to 120.06(6)°, for C14—Sn—C21, is consistent with a trigonal bipyramidal geometry. The non-coordinating Sn···O2 separation is 3.1448(11) Å and consistent with this is the significant disparity in the associated C1—O1, O2 bond lengths, *i.e.* 1.2936(17) and 1.2249(17) Å, respectively.

In the crystal, the only prominent directional intermolecular interaction is a methylene-*C*—*H*···*O*(carbonyl) contact [C21—H21*a*···O2^{iii}: H21*a*···O2^{iii} = 2.48 Å, C21···O2^{iii} = 3.4207(18) Å with angle at H21*a* = 163° for symmetry operation iii: 1 − *x*, 1 − *y*, 1 − *z*]. These contacts serve to link centrosymmetrically chains into double chains.

The title compound has also been characterized as a hydrate with one water molecule per repeat unit [12]. This, too, is a linear coordination polymer. The difference in the structures relates to the Sn—O bond lengths which are each slightly longer in the hydrate, *i.e.* Sn—O1, O2 = 2.189(4) and 3.170(5) Å. Despite crystallizing as a hydrate, no apparent role is evident for the water molecule in the molecular packing. There are eight other structures of the general formula $R_3Sn(O_2CC_5H_4N\text{-}4)$ in the crystallographic literature [13] and each follow the trends established herein. It is noteworthy that the *R* = cyclohexyl compound [14] adopts the common motif but that the Sn—N bond length is long at 2.662(3) Å *cf.* 2.5240(12) Å in the title structure, as is the Sn···O2 separation of 3.345(3) Å, reflecting the influence of the bulky tin-bound substituents.

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